

Blended Polyphosphazene Membranes for Direct Methanol Fuel Cells: Membrane Fabrication

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Preliminary fabrication and characterization studies have shown that ion-exchange membranes composed of crosslinked and sulfonated poly[bis(3-methylphenoxy) phosphazene] possess the required high proton conductivity and low methanol diffusivity properties for direct methanol fuel cells (1-3). Recently, membranes have been prepared by blending sulfonated poly[bis(3-methylphenoxy) phosphazene] (henceforth denoted as SPOP, where the repeating monomer unit is shown in Fig. 1) with either Kynar 761 poly(vinylidene fluoride) or Kynar FLEX™ (a copolymer of vinylidene fluoride and hexafluoro propylene). Both Kynar polymers are made by Elf Atochem. Proton conducting membranes with a substantial Kynar 761 or Kynar FLEX content are attractive for direct methanol fuel cells because: (i) The mechanical properties of the blended film are improved, (ii) the thermoplastic properties of the two Kynar polymers will make hot-pressing electrodes easier during MEA fabrication, (iii) membranes high in Kynar FLEX or Kynar 761 should have a low methanol crossover because these polymer components restrict SPOP swelling and are virtually impermeable to water and methanol, and (iv) the amount of expensive polyphosphazene in the film is low, thus reducing the overall cost of the membrane.

Experimental

Membranes were prepared by sulfonating poly[bis(3-methylphenoxy)phosphazene] (700,000 MW) with SO₃ (4). The resulting polymer was: (i) purified and pretreated in acid, base, and water (4), (ii) dried thoroughly, (iii) mixed with a known weight of either Kynar 761 or Kynar FLEX in dimethylacetamide solvent, and (iv) solution cast into membranes with a dry thickness of approximately 100 μm. Some membranes were crosslinked in dry-film form using electron beam radiation (at Science Research Laboratory, Inc.). Blended and blended/crosslinked membranes were characterized in terms of equilibrium water swelling at 25°C, proton conductivity in water (using an AC impedance method) and methanol diffusivity at 25°C (using a NMR tracer desorption method described in Reference 3).

Results

Water swelling and methanol diffusion coefficient results for a series of different SPOP/Kynar 761 membranes (non-crosslinked) are shown in Fig. 2, where the ion-exchange capacity (IEC) of the SPOP in the blend was held constant at 1.8 mmol/g and the percentage of Kynar was varied between 50% and 80%. Water swelling is in the range of 12-25% and increases with SPOP content. Proton conductivity in these membranes also increased with SPOP

content (e.g., 0.004 S/cm at 50% SPOP and 0.015 S/cm at 80% SPOP). For all of the blended membranes, the methanol diffusivity was very small (< 4.0 x 10⁻⁸ cm²/s as shown in Fig. 2) and consistent with that measured in prior studies (1,3). Proton conductivity vs. temperature results are listed in Table 1 for a blended 75% SPOP/25% FLEX membrane (with an effective IEC of 1.2 mmol/g) that was crosslinked with electron-beam radiation. Additional examples of blended film compositions and properties will be presented in this talk.

Table 1 - Proton Conductivity of a crosslinked 75% SPOP (1.6 IEC)/25% FLEX membrane in water.

Temp (°C)	25	40	50	70
Cond. (S/cm)	0.014	0.018	0.022	0.027

Acknowledgments - This work was funded by the Army Research Office, Grant No. DAAD19-00-1-0517, and by Army Research Office STTR program, through a grant to Science Research Laboratory, Inc. with subcontracts to Tulane University and Northeastern University.

References

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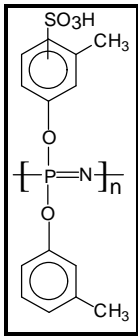


Fig. 1 - Repeating monomer unit of sulfonated poly[bis(3-methylphenoxy)phosphazene].

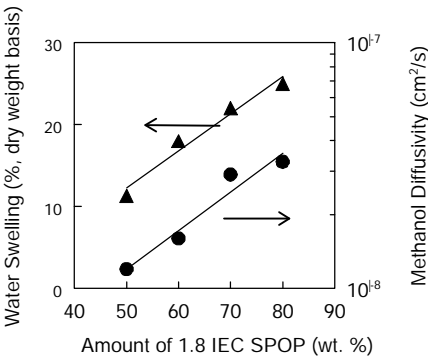


Fig. 2 - Equilibrium water swelling and methanol diffusion coefficients (for 1.0 M methanol) at 25°C for non-crosslinked SPOP/Kynar 761 membranes.